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Spin-Restricted MBPT and CC Theory

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Coupled Cluster calculations for open-shell systems with an unrestricted Hartree-Fock reference (UHF) are usually suffering from spin contamination and are too expensive (by a factor of 3 to 4) in comparison to the corresponding restricted Hartree-Fock (RHF) calculations. Szalay and Gauss (J. Chem. Phys. **107** [1997] 9028) proposed a solution to both problems via the so-called spin restricted (SR) theory, i.e. an approach that introduces additional constraints via projected spin equations. These constraints lead to a reduction of the number of independant amplitudes and thus allow a reduction of the computational effort (within an efficient implementation). Additionally, the CC spin expectation value is equal to the exact spin expectation value even though the wavefunction is not rigorously spin adapted.
In this work we present the extension of the SR-CC-approach — which has initially been derived and implemented only for doublet cases — to triplet- and quartet-cases. Furthermore, analytical gradients for the SR-CC approach are presented along with a „spin-restricted“ variant for many-body perturbation theory (MBPT). Exemplary calculations demonstrate the quality of the results that can be achieved with SR-CC and SR-MBPT.